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THE SYNTHESIS OF UNSATURATED FLUOROCARBONS

64-4

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## I. INTRODUCTION

The purpose of this project is to conduct the necessary research for the preparation of unsaturated organic compounds containing fluorine and, when synthetic methods have been developed, to prepare various fluoroolefins which may give elastomers which are oil and fuel resistant and which retain their elasticity at low temperatures.

It is estimated that 98% of the work has been completed to date and that 96% of the estimated costs have been incurred to date.

This research is authorized under Contract Number DA-19-129-QM-500 and is a further continuation of the work initiated under DA-44-109-QM-522 and continued under DA-44-109-QM-1469. The Wright Air Development Center has contributed funds for the operation of the project in part since September 13, 1956 under MIPR 33(616)-5701.

This is the 29th quarterly report under the contract but the 46th since the project was initiated in 1951. The period covered is from September 13, 1962 through December 13, 1962.

## II. SUMMARY OF CURRENT PROGRESS

A study has been made of the reaction of sodium nitrosyl with hexafluorobenzene but no nitrosopentafluorobenzene was formed.

Two silanes containing the trifluorovinyl group have been synthesized. One of these,  $\text{CF}_2=\text{CF}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$  has been treated with NOCl but no nitroso compound was formed.

Gas-phase additions of NOCl with fluoroolefins has been continued.

Trifluorovinyllithium did not react with hexafluorobenzene to give perfluorostyrene.

A study was made of the reaction of perfluoroallyl chloride with mercurous nitrate. Some acryloyl fluoride was obtained but not enough for

a practical synthesis.

Perfluoroallyl iodide has been coupled to 1,5-perfluorohexadiene via the mercury allyl.

### III. DISCUSSION

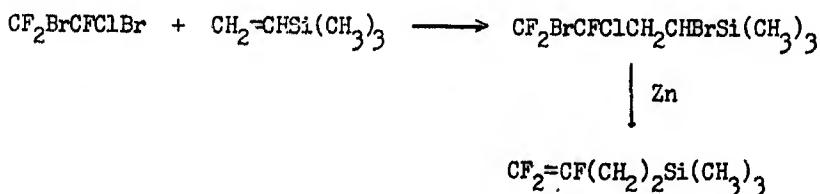
Hexafluorobenzene is known to react with anionic reagents such as methoxide and amide ions to give the methyl ether and the aniline, respectively. It was thought that metal nitrosyl compounds might also react by replacement of fluorine to give the corresponding perfluorophenyl nitroso compound.

Sodium nitrosyl was prepared by the reaction of nitric oxide with a solution of sodium in liquid ammonia. The reaction between sodium nitrosyl and hexafluorobenzene was attempted in ether, methylene chloride and tetrahydrofuran without any evidence of reaction. However, an immediate reaction was noted when a solution of hexafluorobenzene in dimethylformamide was added to a solution of sodium nitrosyl in dimethylformamide. No green or blue color was observed indicating that the desired nitroso compound was not formed. The infrared spectrum indicated that the group attached to the pentafluorophenyl group is large as the spectrum is not dominated by the usual aromatic fluorine absorption peaks associated with this group. It seems most likely that some reaction involving the solvent and hexafluorobenzene has occurred.

Some work has been initiated on the synthesis of fluorine-containing silanes. Earlier requests for nitrososilanes were in part responsible for the initiation of such studies. However, more lately we have been concerned with the synthesis of fluorosilanes as monomers themselves.

It had been anticipated that  $\text{CF}_2\text{ClCFNOCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$  could be prepared by adding  $\text{NOCl}$  to  $\text{CF}_2=\text{CFC}\text{H}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ . It is much easier to work with compounds containing only silicon-carbon bonds and it was decided that the

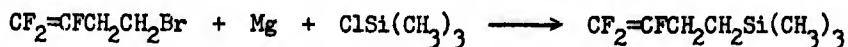
synthesis of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  would be attempted. This material has now been made and characterized. Its synthesis was carried out by the following reaction:



The first step was carried out and a 15% yield of adduct obtained; a larger scale run gave an 80% yield of the adduct. Refluxing the compound with zinc dust and alcohol gave the reduced olefin. The infrared spectrum had a strong peak at  $5.55\mu$  characteristic of the perfluorovinyl group. The NMR spectrum was consistent with that expected for  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ . Elemental analysis was satisfactory.

A small amount of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  was treated with nitrosyl chloride in a sealed tube in sunlight in an attempt to prepare the nitroso compound. The reaction mixture decolorized in 4 hours but no blue material indicative of the desired product was noted. An infrared spectrum of the product showed the presence of the nitro group.

A more direct route to the silane is via the reaction of commercially available  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}$  with trimethylchlorosilane.

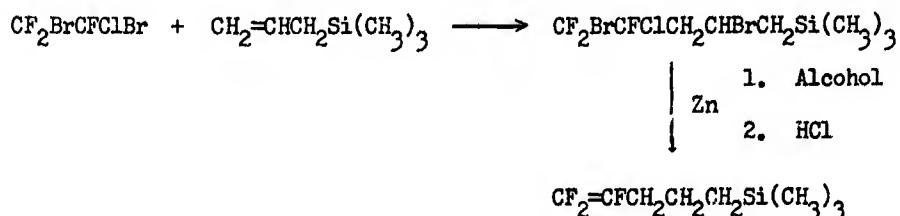


Two procedures were employed in carrying out the reaction. In one, the Grignard was made from the bromide and the chlorosilane then added; in the other, a mixture of bromide and silane were added together. Similar products were obtained in both cases. However, gas chromatographic analysis indicated several products in addition to the starting bromide so the latter

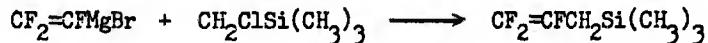
method was not investigated further.

A sample of  $\text{CF}_2=\text{CFSi}(\text{CH}_3)_3$  was made by reaction of trifluorovinylmagnesium bromide with trimethylchlorosilane.

In the near future attempts will be made to prepare  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  and  $\text{CF}_2=\text{CFCH}_2\text{Si}(\text{CH}_3)_3$ . The former is expected to be made via the reaction sequence as shown:



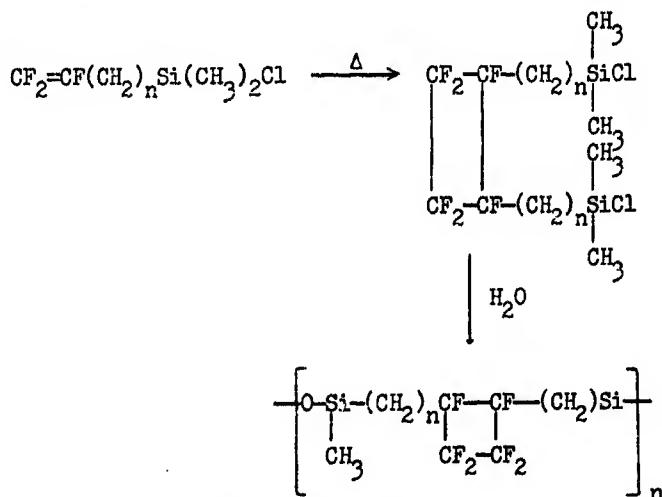
We are hoping that trifluorovinylmagnesium bromide will couple with chloromethyltrimethylsilane to give the desired product.



If these attempts are successful a series of compounds,

$\text{CF}_2=\text{CF}(\text{CH}_2)_n\text{Si}(\text{CH}_3)_3$ , where  $n=0, 1, 2$ , and  $3$ , will be available for further study.

In addition to studying the reaction of such compounds with  $\text{NOCl}$  in an attempt to form nitroso compounds, it is expected that such compounds could lead to interesting products which may be useful in the rubber program. One intriguing possibility is the formation of dichlorosilane with fluorocyclobutane rings in the chain. The following reactions illustrate the synthesis of such materials.



Additional work has been carried out on the sunlight-initiated addition of nitrosyl chloride with fluorolefins. Perfluoro-2-butene reacted to give a mixture of  $\text{CF}_3\text{CFClCF}(\text{NO})\text{CF}_3$  identical with that obtained from the  $\text{AlCl}_3$ -catalyzed reaction reported previously,  $\text{CF}_3\text{CFClCFClCF}_3$  and  $\text{CF}_3\text{CFClCF}(\text{NO}_2)\text{CF}_3$ . According to NMR the nitro compound was present in equal amounts as the threo and erythro isomers.

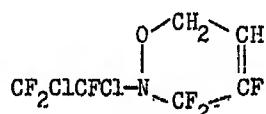
The gas phase reaction of  $\text{CF}_2=\text{CFCOF}$  gave a small amount of blue liquid. This liquid, according to infrared, was a mixture of starting material and nitroso derivative. The mixture was reacted with 1,1,2-trifluorobutadiene. The analysis of the product was different from that of the expected oxazine.

The reaction of nitrosyl chloride and  $\text{CF}_2=\text{CHCF}_2\text{Cl}$  was investigated and found to be complex. Since the liquid fraction was found to contain 7 major components according to gas chromatography, the reaction was not investigated further.

The nitroso compound prepared by adding  $\text{NOCl}$  to perfluoropropene formed the corresponding Diels-Alder product with  $\text{CF}_2=\text{CF}-\text{CH}=\text{CH}_2$  and with butadiene.

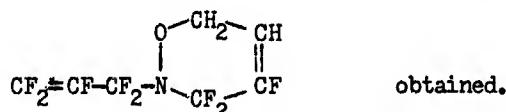
Earlier attempts to reduce  $\text{CF}_2\text{ClCFClNO}_2$  with zinc and hydrochloric acid gave no conclusive evidence of the formation of the desired nitroso compound.

Usually a blue product was obtained but it could not be identified. However, the presence of  $\text{CF}_2\text{ClCFClNO}$  has been proved by reacting the blue liquid with 1,1,2-trifluorobutadiene to give the oxazine,



identical, according to IR and NMR, to an authentic sample.

Earlier results indicated that  $\text{CF}_2=\text{CFCF}_2\text{NO}$  reacted violetly with  $\text{CF}_2=\text{CFCH=CH}_2$ . Since then the procedure has been modified and the expected



#### IV. EXPERIMENTAL

##### Attempted Reaction between Hexafluorobenzene and Sodium Nitrosyl

The sodium nitrosyl was prepared by the method of Zintle and Harder [Ber., 1933, 66, 760]. A concentration of sodium (1 g.) in liquid ammonia (ca. 300 ml.) was found to be dilute enough to give a smooth reaction without risk of explosion.

Preliminary Experiments. Attempts to obtain a reaction between hexafluorobenzene and sodium nitrosyl under reflux conditions in the following solvents were unsuccessful. (1) Ether. (2) Methylene chloride. (3) Tetrahydrofuran.

Reaction in dimethylformamide. Hexafluorobenzene (2.25 g.) in dimethylformamide (7 cc) was added dropwise to a stirred suspension of sodium nitrosyl (0.8 g.) in dimethylformamide (7 cc), preheated for 30 minutes in an oil bath at 60°. There was an immediate indication of a reaction in that the solution turned brown. The mixture was maintained at 60° for 4 hours and

then poured into dilute hydrochloric acid (100 cc). An organic layer shown to be hexafluorobenzene (0.4 g.) separated out. A positive indication of the presence of fluoride ion was shown with cerous nitrate. The aqueous solution was then continuously ether extracted for 24 hours, the ether solution was dried ( $MgSO_4$ ), and evaporated to low volume. The product was separated by gas chromatography (silicone elastomer packing; 30 mm tube;  $140^\circ C$ ) to give a pale straw colored liquid, (0.65 g.).

Partial characterization of compound from the above reaction.

(1) Infrared analysis

Absorption bands at  $3.4 \mu$ , and at  $6.55$  and  $6.61 \mu$  indicate the presence of C-H bands and an aromatic structure respectively.

Further strong bands at  $5.82$  and  $6.08$  indicate the possibility of an unsaturated substituent.

Slight absorption between  $2.9 - 3.1 \mu$  indicated the possibility of an -OH group.

(2) Elemental analysis

Evaluative elemental analysis indicated the presence of nitrogen and fluorine in the molecule.

(3) Test for phenolic group

No derivatives were obtained, and it was concluded that no -OH group was present.

The Preparation of  $CF_2=CFCH_2CH_2Si(CH_3)_3$

$CF_2BrCFClBr$  (10 g.) was placed in a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. The remainder of the fluorine compound was mixed with 25 g. (1/4 mole) of trimethylvinylsilane and 1 g. benzoyl peroxide in the dropping funnel.

The flask was heated to reflux and the mixture slowly added. Refluxing

was continued for six hours. The volatile material was distilled. Seventeen grams of the trimethylvinylsilane was recovered. After much of the excess fluorine compound was removed, the mixture was distilled under vacuum. The desired product  $(\text{CH}_3)_3\text{SiCHBrCH}_2\text{CFCl}$  came over at  $60^\circ/2\text{mm}$ . A yield of 25 g. was obtained.



Ten grams of this compound was refluxed for four hours with zinc dust in ethanol. At the end of this time, 10 ml. conc. HCl was added over a period of time. An oily layer separated. After an hour of reflux, an excess of water was added and the mixture extracted with ether. After several washings, the ether layer was dried over  $\text{MgSO}_4$ . The solution was then concentrated by distilling much of the ether. The product was removed under vacuum, b.p.  $65-67^\circ/125\text{ mm}$ .  $n_D^{18} 1.3835$ . Calculated for  $\text{C}_7\text{H}_{13}\text{SiF}_3$ . C=46.12%, H=7.19%. Found: C=47.15%, H=7.30%. IR had a strong peak at  $5.55\ \mu$  which indicated the presence of the trifluorovinyl group; NMR showed that the hydrogens agreed with the proposed compound  $[(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CF=CF}_2]$ .

A second run was carried out on a larger scale and 68 g. of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  was obtained.

#### The Reaction of $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ with NOCl

An eight mm. glass tube, 20 cm. in length was sealed on one end and charged with 1/4 ml. of silane and 1/4 ml. NOCl. The tube was placed in the sunlight and checked periodically. At the end of four hours, the brown color had disappeared and the solution was colorless. A small amount of insoluble liquid was observed in the tube.

The tube was opened and a large amount of gas escaped. Presumably NO. The liquid was heated to expell any NO and a sample run through the V.P.C. No starting material remained; IR showed a max. at  $6.28\ \mu$ , indicative of NO or  $\text{NO}_2$ . Since there was no blue color, it is assumed that the nitro compound was formed.

Attempted Dimerization of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$

One-half ml. of the silane was placed in a six mm. tube, ten cm. long. The tube was evacuated and sealed and heated at 200° for ten hours. The sample was then removed. The color was not light brown, but V.P.C. showed no high boiling products and only a few low boiling products. The silane was largely unchanged.

Preparation of  $\text{CF}_2=\text{CFSi}(\text{CH}_3)_3$

Trifluorovinylolithium was prepared by dissolving 0.14 mole  $\text{CF}_2=\text{CFBr}$  in 50 ml. ether cooled to -78° in a three-necked flask. To this cooled solution was added 100 ml. of 1.4 N methylolithium solution slowly, alternating with trimethylchlorosilane so that the lithium reagent was always in excess. The mixture was stirred at -78° for a short time and allowed to come to room temperature.

Most of the ether was then distilled off through a column packed with glass helices. The residue was then distilled through a spinning band column. A fraction from 63°-67° was collected, yielding 2.56 g. product. The residue was then removed to continue distillation from simple apparatus. As the residue was heated to boiling again, the mass ignited and a small explosion ensued.

The explosion may have been due to the unhydrolyzed trifluorovinyl-lithium, since similar occurrences have been noted with a reaction mixture containing trifluorovinylolithium.

The yield was 2.6 g. (8.2%), b.p. 63-67°,  $n_D^{20}$  1.3610. A sample purified by V.P.C. had  $n_D^{20}$  1.3565.

The Reaction of NOCl with Olefins

(1) With perfluorobutene\*2. In a typical reaction, a 2-liter flask was evacuated and charged with 350 mm. pressure of olefin and 300 mm. of nitrosyl chloride. After irradiation by sunlight for 5 hours, the products

were separated. The products identified were  $\text{CF}_3\text{CFClCF}(\text{NO})\text{CF}_3$ ,  $\text{CF}_3\text{CFClCFCl--CF}_3$ , and  $\text{CF}_3\text{CFClCF}(\text{NO}_2)\text{CF}_3$ . The nitroso compound was identical with that previously prepared in an  $\text{AlCl}_3$ -dimethylformamide system. The nitro compound was shown by NMR to be almost an equal mixture of erythro- and threo- isomers. Anal. Calcd. for  $\text{C}_4\text{O}_2\text{NClF}_8$ : %C, 17.05; %F, 53.99. Found: %C, 18.38; %F, 53.12.

Analysis by NMR indicated no change in the ratio of cis- to trans- isomers of the olefin recovered.

(2) With perfluoroacryloyl fluoride. A 2-liter bulb was evacuated and then filled with 50 mm. of olefin and 60 ml. of nitrosyl chloride. After 2 hours of sunlight irradiation, 30 mm. of dry air was introduced, and the mixture then was shaken for 2.5 hours with mercury. About 0.3 ml. of blue material was obtained which was indicated by its infrared spectrum to be a mixture of starting olefin and nitroso product. This crude mixture was reacted with diene as will be described later.

(3) With 2-H-3-chlorotetrafluoropropene. A 3-liter bulb was filled with 320 mm. of nitrosyl chloride and 325 mm. of olefin. After 12 hours of sunlight irradiation the gas mixture was still brown, but a colorless liquid had collected in the bottom of the flask. Gas chromatography indicated this material to be a mixture of about seven major products which cannot be separated by distillation and are difficult to separate by V.P.C.

(4) With 1,1,2-trifluorobutadiene. Equimolar amounts of nitrosyl chloride and the diene had reacted completely after half an hour of sunlight irradiation and appears to have given an oxazine and possibly an oxime. Work is still being done on these products.

#### The Reaction of 1,1,2-Trifluorobutadiene with Nitroso Compounds

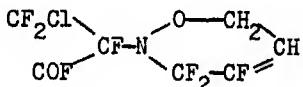
(1) With  $\text{CF}_2=\text{CF}-\text{CF}_2\text{NO}$ . It has been noted that this nitroso compound appeared to react violently with the diene. The reaction was therefore

repeated under different conditions. 1,1,2-Trifluorobutadiene (1.35 g., 0.012<sup>2</sup> mole) and the nitroso compound (1.3 g., 0.0081 mole) were sealed under vacuum in a 140 ml. heavy-walled Pyrex tube at -196°. The tube was then transferred to a bath at -78° which was allowed to slowly warm to room temperature. Distillation of the clear product yielded 0.75 g. (0.0037 mole, 45%) of  $\text{CF}_2=\text{CFCF}_2-\text{N}(\text{O})-\text{CH}_2-\text{CH}(\text{CF}_2)=\text{CF}_2$ .  $n_D^{23} = 1.3605$ .

The structure was confirmed by its IR and NMR spectra.

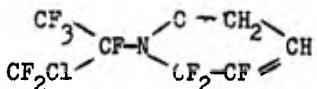
Anal. Calcd. for  $\text{C}_7\text{H}_3\text{ONF}_8$ : %C, 31.24; %H, 1.11; %N, 5.20; %F, 56.46. Found: %C, 31.41; %H, 1.14; %N, 5.10; %F, 56.68.

(2) With  $\text{CF}_2\text{ClCF}(\text{NO})\text{COF}$ . The crude nitroso product was reacted with 1,1,2-trifluorobutadiene. The expected product was



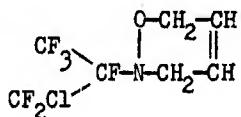
Anal. Calcd. for  $\text{C}_7\text{H}_3\text{ONClF}_7$ : %C, 27.85; %H, 0.995; %F, 44.10. Found: %C, 27.55; %H, 2.49; %F, 28.50.

(3) The product from the reaction of  $\text{CF}_3\text{CF}(\text{NO})\text{CF}_2\text{Cl}$  with 1,1,2-trifluorobutadiene was shown by NMR to have the structure



Anal. Calcd for  $\text{C}_7\text{H}_3\text{ONClF}_9$ : %C, 25.97; %H, 0.93; %F, 52.86. Found: %C, 25.93; %H, 1.06; %F, 52.90.

The structure of the product for  $\text{CF}_3\text{CF}(\text{NO})\text{CF}_2\text{Cl}$  and butadiene was also confirmed by NMR as



Anal. Calcd. for  $C_7H_6ONClF_6$ : % C, 31.17; % H, 2.23; % F, 42.30. Found: % C, 31.27; % H, 2.37; % F, 42.41.

#### The Reduction of $CF_2ClCFClNO_2$

The compound was treated with zinc dust, zinc chloride and ethanol. A blue product was obtained. It was reacted with an excess of 1,1,2-trifluorobutadiene to give the oxazine identical according to infrared and NMR spectra with the oxazine obtained from  $CF_2ClCFClNO$ . This indicated reduction of the  $-NO_2$  to  $-NO$  had taken place.

The reduction was repeated and the nitroso compound again obtained, but the yield appeared to be about 10-15%.

#### Reaction of Perfluoroallyl Chloride with Mercurous Nitrate

Method A. A 2 liter Pyrex flask containing mercurous nitrate (90 g.) and perfluoroallyl chloride (3.33 g., 0.02 mole) was shaken in the dark for 2 hours. Volatile material isolated (3.14 g.) was shown by analytical V.P.C. (dibutyl sebacate 23°C) to be recovered perfluoroallyl chloride; this was confirmed by its infrared spectrum.

A similar reaction was carried out using a mixture of mercury and mercurous nitrate prepared from mercury and nitrogen dioxide. Only recovered starting material (3.3 g.) was isolated.

Method B. Perfluoroallyl chloride (16 g., 0.096 mole) and a mixture of mercury (10 mls.), and mercurous nitrate (25 g., 0.095 mole) were sealed under vacuum in a 40 ml. thick-walled Pyrex tube and shaken at 130° for 24 hours. Volatile material was removed under vacuum and separated by large scale V.P.C. into recovered perfluoroallylchloride (8.0 g., 50% conversion), hexafluoropropene (4.5 g., 62.5% yield), and perfluoroacryloylfluoride (0.3 g., 5% yield). The identity of all three compounds was established by comparison of their infrared spectra with authentic samples.

The infrared spectrum of both starting and recovered perfluoroallyl

chloride indicated a mixture of 2 or more compounds but no complete resolution could be made by V.P.C. or distillation. The impurities would undoubtedly be chlorofluoropropanes or propenes and should not interfere in the reaction of the perfluoroallyl chloride with mercurous nitrate.

A similar reaction was carried out at 130° using only mercurous nitrate and perfluoroallyl chloride. Approximately the same amounts of recovered starting material and hexafluoropropene as in the previous reaction were obtained. No perfluoroacryloyl fluoride was formed.

Similar reactions carried out at 80-85° resulted in no conversion of the perfluoroallyl chloride.

#### Reaction of Trifluorovinylolithium with Hexafluorobenzene

Bromotrifluoroethylene (14.1 g., 0.1 mole) in pentane (50 mls.) was cooled in a bath at -78°C and treated simultaneously with a solution of n-butyllithium (64 mls., 1.56 N sol., 0.1 mole) and hexafluorobenzene (18.6 g., 0.1 mole) in pentane (25 mls.). The period of addition was 30 minutes.

The reaction mixture was then allowed to slowly warm to room temperature. At -78°C to -40°C the sol. was cloudy but almost colorless. However at -40°C to -25°C it gradually became darker as all unreacted trifluorovinyllithium polymerized.

3N hydrochloric acid (50 mls.) was slowly added with shaking and the separated organic layer was washed with water (3 x 50 mls.) and dried over Drierite.

Pentane and some hexane was removed by distillation through an 18" nickel gauze packed column. The residue was distilled through a spinning band column giving fractions of boiling range 67°-68°, 80°-100°, and 100°-100.5°C. The first fraction was shown by infrared spectroscopy to contain both hexane and perfluorobenzene. This was confirmed by analytical V.P.C. The next two fractions also contained some hexane, hexafluorobenzene and

some n-butyl bromide. The last fraction was pure n-butyl bromide. The residue from the distillation was vacuum distilled from a bath at 100°C at a pressure of  $10^{-3}$  mm/Hg. The distillate was shown by analytical V.P.C. (silicone elastomer 140°C) to contain mainly n-butyl bromide together with two less volatile components. An infrared spectrum of this last fraction showed a small triplet peak 5.55, 5.70 and 5.81  $\mu$  which indicated the presence of some perfluorostyrene. All of this fraction was separated by large scale V.P.C. into n-butyl bromide and a mixture of the other two components. The latter consisted only of a smear on the sides of the trap and was insufficient even for the recording of its infrared spectrum.

No estimate of unreacted hexafluorobenzene was made due to a partial merging of peaks on analytical V.P.C. with one peak of commercial hexane. The total amount of n-butyl bromide was estimated from the pure material obtained and by peak area measurements in impure samples to be 11.5 g. (84% yield).

#### Preparation of 1,5-Perfluorohexadiene

Perfluoroallyl iodide (6.5 g., 0.0252 mole) and mercury (3 mls.) were sealed under vacuum in a 40 ml. Pyrex tube and shaken under irradiation from a Hannovia SH ultra-violet burner for 2 1/2 days. Volatile material was isolated under vacuum and introduced onto a large scale V.P.C. column (dinonyl phthalate 50°). Only the main component was isolated and identified as decafluoro-1,5-hexadiene (1.5 g., 45.5% yield). Calcd. for  $C_6F_{10}$ : mol. wt., 262. Found: mol. wt. 260.

An infrared spectrum showed C=C stretching absorption at 5.6 (*s*)  $\mu$  and bands at 7.35 (*s*), 7.6 (*s*), 8.4 (*s*), 9.13 (*s*), 9.8 (*w*), 10.1 (*m*), 11.2 (*ms*) and 11.8 (*s*)  $\mu$ .

#### V. FUTURE WORK

Research will be continued on the synthesis of silanes containing the  $\text{CF}_2=\text{CF}-$  group.

Research will also be carried out on the reaction of fluoroallyl ketones with polyhydric alcohols to obtain ketal polymers containing fluorine.

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#### V. FUTURE WORK

Research will be continued on the synthesis of silanes containing the  $\text{CF}_2=\text{CF}-$  group.

Research will also be carried out on the reaction of fluoroallyl ketones with polyhydric alcohols to obtain ketal polymers containing fluorine.

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